Appendix M

Conjugated Oligomers, Their Assembly on Gold, and Their Uses in Molecular Electronics Studies

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Organic compounds have the potential to serve as molecular components of electronic devices.[1] As a prelude to the design of such devices, it is valuable to understand electrical conduction through single or small arrays of conjugated organic molecules that might ultimately serve as molecular wires.[2] Here we describe studies of self-assembled monolayers (SAMs) derived from a series of sulfur-terminated conjugated oligomers (Table 1).[3] The purpose of this study was to establish the geometry and density of packing of these materials, in order to use them in evaluation of molecular conduction.[4,5] Additionally, we present here preliminary conduction study data across some of these single molecules, or small arrays of molecules, using a tip-to-tip STM configuration (mechanical break-junction).

Figure 1 compares the thickness of the SAMs estimated by ellipsometry versus the actual molecular lengths calculated by molecular mechanics.[6] Figure 2 indicates the extent of correlation between the data from the X-ray photoelectron spectroscopy (XPS) and ellipsometry. The inference from the data is that these thiols form monolayers (at 0.1-1.0 mM in THF) whose thickness corresponds to the extended, end-to-end distance of the (di)thiol. In some cases, the thickness suggested that the organic compounds are nearly normal to the surface.

Table 1. Sulfur-terminated oligomers.

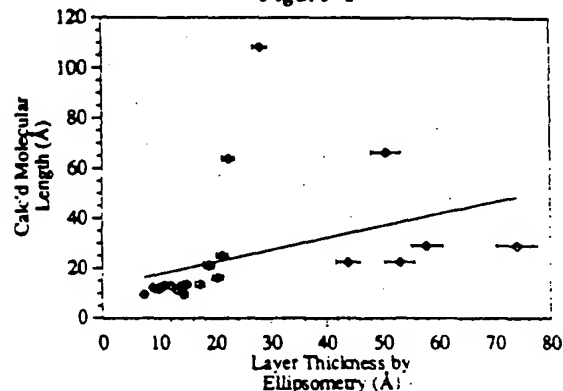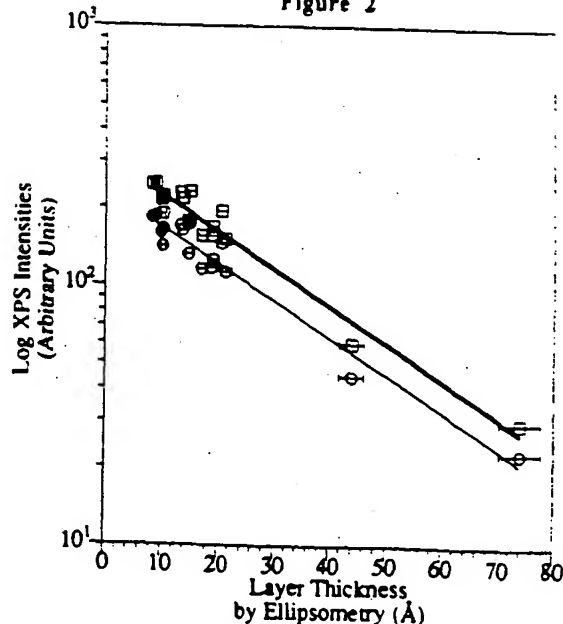| Structure	R, R'
R—⬡—R'	HS, SH AcS, SAc
R—⬡—⬡—R	H, SH H, SAc HS, SH AcS, SAc
TMS—≡—⬡—R	SH SAc
R—⬡—≡—⬡(Et)—≡—⬡—R'	H, SH H, SAc HS, SH AcS, SAc
R—⬡—≡—[⬡(Et)—≡]₂—⬡—R'	HS, SH AcS, SAc
⬡(S)—⬡(S)—R	SH SAc
TMS—[≡—⬡(Et,S)]₂—≡—⬡—R	SAc
TMS—≡—⬡(Et,S)—≡—⬡—R	SAc
H—[⬡(Et,S)—≡—⬡]₁₆—R	SAc
R—⬡—≡—[⬡(Et,S)]₈—≡—⬡—R'	AcS, SAc

Figure 1

Figure 2. Log of the XPS intensities from organic-covered Au substrates versus the organic layer thickness measured by ellipsometry [Au(4f7/2) (squares) and Au(4f5/2) (circles)]. One scan was used to minimize damage effects over a 15 eV window.

Neither the presence of the aryl groups (with their potential absorbing π and thiophene sulfur centers) nor of the second thiol group, seems to influence the mode of adsorption in several of the systems investigated.

Aromatic thiols oxidize readily, and previous work with flexible α,ω-dithiols has suggested that they tend to form multilayers, presumably via disulfide linkages.[7] Acetyl-protected thiols provided an excellent method to alleviate the problems in isolating and using the oxidatively unstable thiols. In the cases where monothiol-containing systems (ArS) were needed, we could have used disulfides (Ar-SS-Ar) as precursors;[4] this strategy, however, is impractical for the α,ω-dithiols, since successive oxidative oligomerization would generate insoluble poly(disulfides). ^{1}H NMR and ^{13}C NMR analysis in THF-d₈ showed that an aryl thioacetate could be deacylated completely within 10 min using aqueous NH₄OH.[8] Other bases such as DMAP or dipropylamine were far less effective. NH₄OH-promoted removal of alkynyl-TMS groups was not observed within 72 h. Therefore, in situ deprotection of the acetyl moieties could be carried out using NH₄OH (aq) to form SAMs. The thioacetyl moiety could even be used, without deprotection using exogenous base, to generate the SAM directly, though higher concentrations (30-40 mM in THF) of thioacetates relative to thiols were required to achieve monolayer coverage. We have not determined the mechanism of the adsorption though hydrolysis of the thioesters via trace amounts of water or enol forms of the thioesters are plausible reactions. This method of direct adsorption of α,ω-dithioacetyl compounds results only in monolayer formation: there was no multilayer formation as was observed in the free dithiols.

Formation of SAMs from these rigid-rod compounds is slower than with n-alkanethiols. As the oligomers become larger, monolayer formation becomes slower, though the linear oligo(phenylene ethynylene)s appear to adsorb more efficiently than the nonlinear oligo(thiophene ethynylene)s. In the case of the longer oligo(thiophene ethynylene)s, the SAMs are significantly shorter than expected (Figure 1), based on the lengths of the starting material, and we can not exclude the possibility of competitive adsorption by thiol and thiophene groups.

For the conductivity studies across a single molecule (or possibly a small array of molecules), we used a gold mechanical break-junction tip-to-tip STM device (Figure 3)[9] to record conductivities across what may be a single molecule. The I(V) characteristics across 1,4-benzene dithiol are shown in Figure 4. Though further studies are underway, this preliminary data suggests that single molecules may provide a viable conduction pathway with current capabilities in a usable electronic regime. These results pave the way for further research into the feasibility of molecular electronics.

References and Notes

[†]Surface studies conducted while on sabbatical leave at Harvard University.

(1) (a) Molecular Electronics· Science and Technology. Aviram. A., Ed.: Confer. Proc. No. 262, American Institute of Physics:

New York, 1992. (b) Molecular Electronic Devices II; Carter, F. L., Ed.; Marcel Dekker: New York, 1984. (c) Miller, J. S. Adv. Mater. 1990, 2, 378, 495, 601. (d) Waldeck, D. H.; Beratan, D. N. Science 1993, 261, 576.

(2) (a) Nanostructure Physics and Fabrication, Reed, M. A.; Kirk, W. P., Eds.; Academic Press: San Diego, 1989. (b) Nanostructures and Mesoscopic Systems, Kirk, W. P.; Reed, M. A., Eds.; Academic: San Diego, 1992.

(3) For the preparations of the extended oligomers, see: Schumm, J. S.; Pearson, D. L.; Tour, J. M. Angew. Chem. Int. Ed. Engl. 1994, 33, 1360. Pearson, D. L.; Schumm, J. S.; Tour, J. M. Macromolecules 1994, 27, 2348.

(4) Chang, S.-C., Chao, I.; Tao, Y.-T. J. Am. Chem. Soc. 1994, 116, 6792.

(5) For an overview on SAMs, see: Ulman, A. An Introduction to Ultrathin Organic Films, Academic: Boston, 1991.

(6) Modified MM2 force-field, version 3.7, from CAChe Scientific Inc.

(7) Bain, C. D.; Whitesides, G. M. J. Phys Chem. 1989, 93, 1670.

(8) Ponticello, G. S.; Habecker, C. N.; Varga, S. L.; Pitzenberger, S. M. J. Org. Chem. 1989, 54, 3223.

(9) Krans, J. M.; Muller, C. J.; Yanson, I. K.; Govaert, T. C. M.; Hesper, R.; van Ruitenbeek, J. M. Phys. Rev. B 1993, 48, 14721.
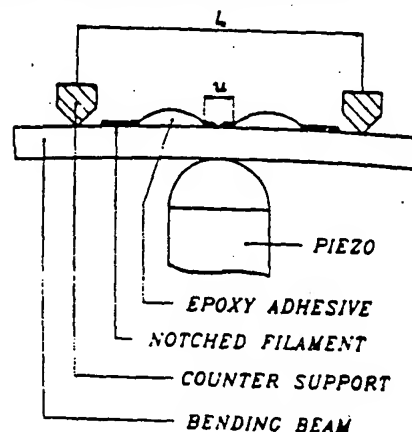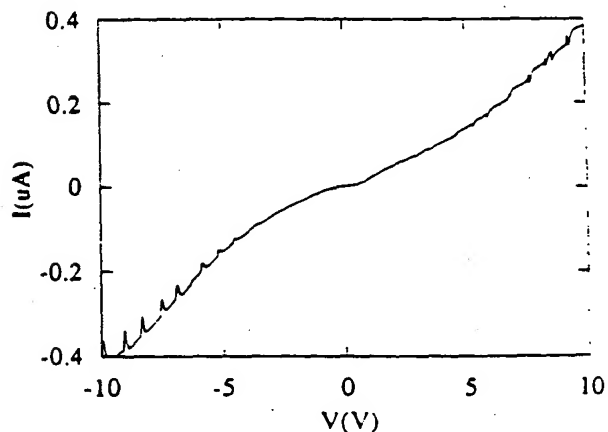
Figure 3. Mechanical break junction.

Figure 4

I(V) curve from the mechanical break junction after evaporation of a THF solution of 1,4-benzenedithiol. Probes held at 7.6 Å.